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Zhurnal Obshchey Khimii, Vol XX (LXXXII), No 1, 1950. Doklady Akademii Nauk SSSR Vol LXXII, No 1, 1950

RECENT WORK ON ORGANIC TIN COMPOUNDS,
SIMILAR DERIVATIVES OF OTHER ELEMENTS,
AND THE SYNTHESIS OF TIN-PHOSPHORUS COMPOUNDS

While the toxicological properties of the newly synthesized tin-phosphorus compounds mentioned below have not been published by the Russian authors, it may be assumed that some of these substances have a strongly toxic effect. A sternutatory effect combined with physiological action, commonly ascribed to phosphorus derivatives of this type, is conceivable.

The tin-phosphorus compounds on which data has been published in this instance have high melting points and presumably low volatility. However, if found to possess appropriate toxicological properties, they can presumably be used as in the form of aerosols. No actual intention to use compounds of this type in the manner mentioned above is implied -- this is entirely conjectural.

In the May 1, 1950, issue of Doklady Akademii Nauk SSSR (Reports of the Academy of Sciences of the USSR), Vol LXII, No 1, A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, G. I. Gavrilov, and E. N. Merkulova published a paper on the synthesis of organic compounds of elements of the IVth Group by using the diazo method. The contents of this paper are summarized below.

Previous work [1] has demonstrated that aliphatic diazo compounds can be used successfully for the synthesis of organic derivatives of Group V elements. The current article describes results of investigating the reaction of aliphatic diazo compounds with halides of Group IV elements.

In the only previous work which has been published so far on the same subject [2], it was noted that tin-organic compounds are not formed as a result of the interaction of tin tetrachloride with diazo acetic ester and diazo methane. The present study shows that halides (chlorides and bromides) of tin, lead, and silicon react with diazo aliphatic compounds to form corresponding alpha-halogen-alkyl derivatives of these elements. The reaction proceeds according to the scheme

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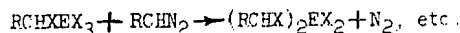
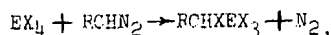
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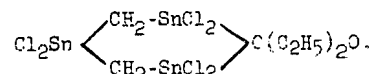
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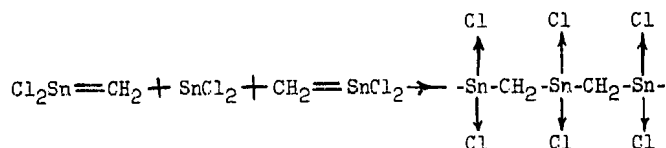
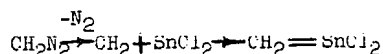
Tin tetrachloride or tetrabromide, at 0-5°C in benzene, readily interact with aliphatic diazo compounds to form all possible alpha-halogen-alkyl derivatives of tin. In this reaction, it is evident that an increase in the number of radicals combined with the metal makes it more difficult to obtain further introduction of the alkylene radical in this manner (alkylenization) so that the formation of tetra-substituted derivatives, for example, generally proceeds very slowly and only in the presence of a considerable excess of the diazo compound. Formation of primary, secondary, and tertiary derivatives occurs simultaneously, the relative amounts of each compounds dependent on the ratio of the diazo compound and the tin halide.

The alpha-halogen-alkyl halides of tin as well as the diazo compounds with other alkylene radicals or magnesium-organic compounds, all of which are used as reagents in these reactions, can be synthesized from mixed alpha-halogen-alkyl tin derivatives containing various alpha-halogen-alkyl radicals or halogen substituted and nonsubstituted radicals. Tin tetrafluoride does not react with diazo aliphatic compounds.

In contrast to tin tetrachloride, stannous chloride reacts with diazo methane in an unusual fashion to form various polystannic derivatives of tetra-valent tin. As a result of conducting this reaction in ether, there was obtained a substance the structure of which, according to its chemical properties and conversion products, is represented by the formula:

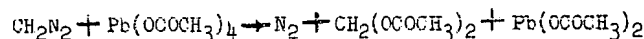


In benzene analogous higher molecular compounds are formed. The interaction of the reagents in this case proceeds, apparently, according to the scheme:



In this reaction polymerization is interrupted through the action of traces of moisture which are present in the reaction medium.

In contrast to the tin halides, lead chloride and the ammonium salt of lead chloride-hydrochloric acid do not react with diazo aliphatic compounds, probably due to the fact that they are practically insoluble in the mediums usually used in these reactions. On the other hand, soluble lead tetraacetate interacting with diazo methane causes an energetic evolution of nitrogen as well as the formation of methylenediacetate and plumbous acetate;



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Alkylenization along the Pb-X bond was observed under specific conditions in reactions of diazo methane with triethyl and diethyl lead chlorides in the presence of copper bronze. Without the catalyst these reagents do not interact even when heated. Copper bronze as well as copper salts cause decomposition of the diazo compound, which leads to the formation of alkylene radicals, and promotes alkylenization with formation of alpha-chloromethyl derivatives of lead. Alpha-chloroethyl compounds were found to be unstable, and their preparation in a pure form was unsuccessful.

At ordinary temperatures aliphatic diazo compounds were very energetically decomposed by silicon tetrachloride or tetrabromide; because of this, the formation of silicon-organic compounds was not observed, the reaction product in this case being a high molecular compound (a polymethylene). That is why the reaction to prepare silicon-organic compounds is conducted at temperatures of -45 to -55°C in an ether solution. The nonsubstituted alkylsilicon halides (CH_3SiCl_3 , $(\text{CH}_3)_2\text{SiCl}_2$) react with aliphatic diazo compounds more slowly than the inorganic halides of silicon or alpha-halogen-alkyl derivatives of silicon.

Since an increase in the reaction temperature in these cases decreases the yields of silicon-organic compounds because of an increase in the quantity of polyalkylenes forming in a secondary reaction, a catalyst -- copper bronze or anhydrous copper sulfate -- is used to accelerate the reaction by decomposing the diazo compound at low temperatures and thereby increasing (10-15 times) the formation of halogen-alkyl-silicon halides.

Tetra-(halogen-methyl)-silanes, decomposed by heating, could not be isolated. Silicon tetrafluoride, energetically interacting with aliphatic diazo compounds with the formation of nitrogen and polymethylene, did not form silicon-organic compounds even at low temperatures. (See Table 1).

Therefore, the interaction of aliphatic diazo compounds with halides of Group IV elements, (as well as with Group V elements) is a convenient new method for the synthesis of elemento-organic compounds, which are difficult to prepare in other ways. The results obtained in this investigation also show that the applicability of the diazo method for the synthesis of elemento-organic compounds of the aliphatic series is no less general than that of the analogous method for the aromatic series.

Experimental data on the reactions of diazo compounds with halides of various elements make it possible to consider these reactions as free radical reactions. The biradical formed in the decomposition of the diazo compound is an alkylene group which is introduced along the E-X bond, this leading to the formation of new elemento-carbon bonds.

Other possible processes in this reaction are: the solvent being attacked by free radicals, the polymerization of alkylenes into polyalkylenes and a reaction with halides of elements at the site of unshared valence electrons of the element, leading to an increase in the valency and formation of new elemento-organic compounds.

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Table 1

Synthesized Alpha-Halogen-Alkyl Derivatives

<u>Formula of the Compound</u>	<u>B.p. in °C</u>	<u>d_{20}^{20}</u>	<u>n_D^{20}</u>
$\text{ClCH}_2\text{SiCl}_3$	116.5°/750 mm	1.4776	--
$(\text{ClCH}_2)_2\text{SiCl}_2$	58.5°/16 mm	1.4624	--
$(\text{ClCH}_2)_3\text{SiCl}$	70°/4 mm	1.4377	--
$\text{CH}_3(\text{CH}_2\text{Cl})\text{SiCl}_2$	121-122°/760 mm	1.2778	--
$\text{CH}_3\text{CHClSiCl}_3$	66°/75 mm	1.3919	--
$\text{BrCH}_2\text{SiBr}_3$	70°/6 mm	2.5730	--
$(\text{BrCH}_2)_2\text{SiBr}_2$	107°/9 mm	2.4614	--
$(\text{BrCH}_2)_3\text{SiBr}$	123°/5 mm	2.3440	--
$[\text{BrCH}_2)_3\text{Si}]_2\text{O}$	m.p. 69.5°	--	--
$\text{ClCH}_2\text{SnCl}_3$	72.5-73°/5 mm	2.21	1.5689
$(\text{ClCH}_2)_2\text{SnCl}_2$	m.p. 89.5-90°	--	--
$(\text{ClCH}_2)_3\text{SnCl}$	138-140°/5 mm	2.03	1.593
$(\text{ClCH}_2)_4\text{Sn}$	m.p. 49-49.5°	--	--
$\text{BrCH}_2\text{SnBr}_3$	109°/5 mm	3.251	--
$(\text{BrCH}_2)_2\text{SnBr}_2$	m.p. 87°	--	--
$(\text{BrCH}_2)_4\text{Sn}$	m.p. 57°	--	--
$(\text{CH}_3\text{CHCl})_2\text{SnCl}_2$	112°/4 mm, m.p. 12°	1.829	1.5535
$(\text{CH}_3\text{CHCl})_3\text{SnCl}$	130°/3 mm	1.684	1.5450
$(\text{CH}_3\text{CHCl})_4\text{Sn}$	142°/2 mm	1.568	1.5365
$(\text{CH}_3\text{CHCl})_2\text{SnO}$	m.p. 180°	--	--
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCl})_2\text{SnCl}_2$	134°/5 mm, m.p. 53°	--	--
$\text{ClCH}_2\text{SnCl}(\text{CHClCH}_3)_2$	128°/3 mm	1.765	1.555
$(\text{ClCH}_2)_2\text{Sn}(\text{CHClCH}_3)_2$	141-142°/5 mm	1.675	1.5478
$(\text{CH}_3\text{CHCl})_2\text{Sn}(\text{C}_2\text{H}_5)_2$	114-115°/5 mm	1.414	1.5083
$(\text{C}_2\text{H}_5)_3\text{PbCH}_2\text{Cl}$	66°/3 mm	1.7917	1.5443
$(\text{C}_2\text{H}_5)_2\text{Pb}(\text{CH}_2\text{Cl})_2$	96°/2 mm	1.9890	--
$(\text{C}_2\text{H}_5)_3\text{PbCHClCH}_3$	decomposes at 20°		

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[It will be noticed that organic tin halides have been synthesized by the method described in the paper published by A. Ya. Yakubovich et al and summarized above. According to B. A. Arbuzov and N. P. Grechkin, Zhurnal Obshchey Khimii (Journal of General Chemistry), Vol. XX (LXXXII), No. 1, January 1950, pp. 107-15, analogous compounds (iodides in this case) react with esters of phenylphosphinous and di-phenylphosphinous acids, yielding the tin-phosphorus organic compounds which are listed below together with data on their properties and details of the reactions leading to them.]

Addition of 2.8 g PhP(OMe)_2 to 4.7 g Me_3SnI and warming to 80°C gave a violent reaction (maximum temperature 240°C) which on subsidence gave 3.4 g PhPO(OMe)_2 (SnMe_3), m. pt. $132-4^\circ\text{C}$ (from EtOH). Similar reaction of 6.4 g PhP(OEt)_2 with 10.8 g Et_3SnI preheated to 150°C gave insoluble colorless PhPO(OEt)_2 (SnEt_3), m. pt. $294-7^\circ\text{C}$, in 1.6 g yield. The use of 4.3 g PhP(OEt)_2 and 9.5 g (Bu_3SnI) at 185°C gave 7.2% insoluble PhPO(OEt)_2 (SnBu_3), m. pt. $302-5^\circ\text{C}$ (decomposition), although 86% EtI was evolved. Heating PhPO(OMe)_2 (SnMe_3) 30 minutes with H_2O gave no change, but 15% HCl at room temperature yields Me_3SnCl rapidly, while 10% KOH in three hours yields Me_3Sn hydroxide, m. pt. $117-20^\circ\text{C}$. Addition of 5.1 g PhP(OMe)_2 to Me_2SnI_2 (6 g) gave after a violent reaction 3.7 g $\text{Me}_2\text{Sn(P(O)(OMe)Ph)}_2$, decomposing at $291-3^\circ\text{C}$. Similarly 7 g Et_2SnI_2 and 6.5 g PhP(OEt)_2 after preheating to 150°C gave 2.8 g $\text{Et}_2\text{Sn(P(O)(OEt)Ph)}_2$, decomposing at $296-300^\circ\text{C}$, while 4.5 g Et_2SnI_2 and 5 g PhP(OPr)_2 gave, at 195°C , 61.4% $\text{Et}_2\text{Sn(P(O)(OPr)Ph)}_2$, decomposing at $245-8^\circ\text{C}$. All these products are insoluble in organic solvents; they are stable to hot H_2O , but rapidly cleave in 15% HCl yielding R_2SnCl_2 , while 10% NaOH yields R_2SnO ; action of Cl_2 in CHCl_3 also yields R_2SnCl_2 at room temperature. Heating PhP(OEt)_2 eight hours in sealed tube to 300°C gave 36% $\text{Ph}_2\text{P(O)Ph}$; this treated with MeOH in presence of Me_2NPh gave 53% Ph_2POMe , b₁₀ $152-5^\circ\text{C}$, while EtOH gave 51% Ph_2POEt , b₁₀ $161-3^\circ\text{C}$. Heating 7 g Et_3SnI and 4.9 g Ph_2POEt to 170°C gave 5.1% $\text{Ph}_2\text{P(O)SnEt}_3$, decomposing at $346-8^\circ\text{C}$, while $\text{EtOH-Et}_2\text{O}$ washings gave Ph_2EtPO , m. pt. $121-4^\circ\text{C}$ (1.4g). Likewise, 5.1 g Me_3SnI and 4 g Ph_2POEt gave 9.8% $\text{Ph}_2\text{P(O)SnMe}_3$, decomposing at $365-8^\circ\text{C}$, and 1.75 g Ph_2EtPO , while 4.6 g Et_3SnI treated with 3 g Ph_2POMe and heated to 190°C gave Ph_2MePO , m. pt. $108-10^\circ\text{C}$, and 4.2 g Et_3SnI (91.5%). Me_2SnI_2 (6 g) and 6.9 g Ph_2POEt heated at 140°C gave 2.2 g $\text{Me}_2\text{Sn(P(O)Ph)}_2$, decomposing at $372-5^\circ\text{C}$, and 0.9 g Ph_2EtPO , while 5.6 g Et_2SnI_2 and 6 g Ph_2OEt gave 17.3% $\text{Et}_2\text{Sn(P(O)Ph)}_2$, decomposing at $351-3^\circ\text{C}$, and Ph_2EtPO . These derivatives are stable to hot H_2O , while warm 15% HCl yields $\text{Ph}_2\text{PO}_2\text{H}$, m. pt. $193-4^\circ\text{C}$, and R_2SnCl_2 , and hot 20% NaOH similarly gives $\text{Ph}_2\text{PO}_2\text{H}$ and R_2SnO ; action of Cl_2 also yields R_2SnCl_2 and presumably Ph_2POCl , for aqueous treatment yields $\text{Ph}_2\text{PO}_2\text{H}$; the action of AcCl in benzene under reflux is similar, as R_2SnCl_2 and $\text{Ph}_2\text{PO}_2\text{H}$ are isolated.

[The paper by A. Ya. Yakubovich et al was submitted for publication on 6 Dec 1949, and presented by Academician A. N. Nesmeyanov on 21 Feb 1950. The paper by B. A. Arbuzov and N. P. Grechkin, which originated by the Chemical Institute of the Kazan Affiliate, Academy of Sciences USSR, was submitted for publication on 8 Jul 1948, according to the note under the published article, and published on the date mentioned above.]

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